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CHANGES IN THE ORIENTATIONS OF THE PRINCIPAL MAGNETIC AXES OF SINGLE CRYSTALS OF THE IRON GROUP OF SALTS WITH VARIATION OF TEMPERATURE*

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ABSTRACT In most of the crystals studied by the author the orientations of the principal magnetic axes were found to change very little with temperature In a few cases the changes were large and are obviously to be attributed to changes in the relative orientations of the different paramagnetic groups present in the unit cell of the crystal, due to the fact that the binding between such groups is comparatively weak The individual members of the paramagnetic groups are bound much more firmly so that these groups persist even in the state of solutions and in consequence the electric field axes associated with each group do not change.

INTRODUCTION

In the course of the investigations on the magnetic behaviour of single crystals of the salts of the iron group it was observed that in a few of the crystals the principal magnetic axes had a tendency to change their orientations when the crystals were subjected to a variation of temperature. Such variations have earlier been observed also by Bartlett (1932) who worked within a limited range of temperatures from about $+50°$ to $-50°$C, for almost all the crystals studied by him. Though a very large number of crystals were investigated by the present author over a large range of temperature and also later by some of his colleagues, they never found any such change for crystals in which the position of the principal magnetic axes are fixed uniquely from crystal symmetry such as the tetragonal, trigonal, hexagonal or rhombic classes as is only to be expected. Even in the triclinic crystal $CuSO_4,5H_2O$ (Krishnan and Mookherji 1938) no such change was observed. Appreciable changes were found only in a few exceptional cases of monoclinic crystals and the present paper deals with the nature and the probable cause of these variations.

METHOD AND RESULTS

The method of observing the settings of the crystal in a magnetic field and their variations is the same as has been used in this laboratory in connection with the measurements of anisotropies of single crystals (Krishnan,

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Mookherji and Bose, 1939). It is obvious that when a crystal is suspended in a homogeneous horizontal magnetic field with a fine quartz fibre from a torsion head, with one of its principal magnetic axes vertical, the other two principal axes will tend to set along and perpendicularly respectively, to the magnetic field, and will actually do so when the torsion head has been adjusted so that there is no torsion on the fibre.

To observe the variations of the orientations of the horizontal axes of the crystal with temperature it was put in a cryostatic device in which any temperature between 300°K and 80°K can be attained and maintained steady (Bose, 1940, 1946). The changes of the orientation of the crystal were noted with the help of an index attached near the middle part of the suspending system, just outside the cryostat chamber, as has been described in these papers. When such changes were observed at different temperatures the torsion head was turned until on putting on the magnetic field there was again no torsion on the fibre, *i.e.*, the crystal had again freely set with its new position of the maximum susceptibility axis along the field. The amount of rotation on the torsion head gives us the change of orientation of the axis. The observations on ten monoclinic crystals were taken by the author at various temperatures between 300 K and 80°K and the results are tabulated in the following tables. The notations adopted are the same as in our earlier papers. The results are for suspensions of the crystals with "*b*" axis vertical.

TABLE I*

For changes of setting in the Magnetic Field

Crystal	Total change in the direction ψ, of χ_1 on passing from 300°K to 80°K
$NiSO_4$, $(NH_4)_2SO_4$, $6H_2O$	$-14°$ to $-19°.25$
$NiSO_4$, K_2SO_4, $6H_2O$	$-12°.5$ to $-13°.5$
$NiBeF_4$, $(NH_4)_2BeF_4$, $6H_2O$	$-14°.3$ to $-13°.3$
$CoSO_4$, $(NH_4)_2SO_4$, $6H_2O$	$-43°.2$ to $-41°.2$
$CoSO_4$, K_2SO_4, $6H_2O$	$-15°.5$ to $-13°.5$
$CoBeF_4$, $(NH_4)_2BeF_4$, $6H_2O$	$-38°.1$ to $-31°.6$
Cs_2CoCl_4 (O: thorhombic)	Nil
$FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$	$+54°.5$ to $+52°.5$
$FeSO_4$, K_2SO_4, $6H_2O$	$+58°.3$ to $+60°.3$

* The initial angle and the changes are measured in sexagesimal degrees.

TABLE II*

$CuSO_4$, A_2SO_4, $6H_2O$

Salts	Initial angle ψ at 300 K	Change in the direction of χ_1 axis with temp as compared with that at 300°K										
		280°	260	240°	220°	200°	180°	160°	140°	120°	100°	80°
A=K	−77° 5	−1 1	− 9	− 9	− 8	− 6	− 5	− 4	− 3	− 2	0	0
A=NH_4	+77° 5	+3 7	+2 3	+1 3	+1 8	+1 7	+1 5	+1 5	+1 3	0	0	0

In the orthorhombic crystal of Cs_2CoCl_4 no changes in the orientation occurred. In addition to these the author observed in an earlier measurement (Krishnan, Mookherji and Bose, *loc. cit.*) no change in orientation in the trigonal crystals of $NiSO_4$, $6H_2O$ and $NiSeO_4$, $6H_2O$, the monoclinic crystals of $MnSO_4$,$(NH_4)_2SO_4$,$6H_2O$ and $Gd_2(SO_4)_3$,$8H_2O$. In the monoclinic crystal of ammonium chromium oxalate, however, with suspension along "b" axis a very large change of "ψ" by about 78° was observed between 303°K and 90°K.

DISCUSSIONS

In the paramagnetic crystals that we are considering, the electric field in the neighbourhood of the paramagnetic ion, which profoundly affects its magnetic behaviour, is known to arise from the negatively charged atoms surrounding the paramagnetic ion (Van Vleck, 1932; Bethe, 1929; Penney and Schlapp, 1932, etc.). It can be seen in a general way that when the atoms are densely packed, as they are in these crystals, the field should be predominantly cubic in its symmetry. Representing the potential, V, of the electron in this crystalline field as a Taylor's series about the centre of the paramagnetic ion, it can be shown that when the field is accurately cubic in symmetry the first non-vanishing terms in the series can be expressed in the convenient form,

$$V = D(x^4 + y^4 + z^4) + 3D_1^4 \qquad \ldots \quad (1)$$

in which the last term corresponding to the spherically symmetric part of the field can be omitted for convenience, since it does not disturb the relative separations of the energy levels, with which alone we are concerned here. On the other hand, if the field deviates from cubic symmetry by having a small rhombic field superposed on the cubic, the first non-vanishing terms in the expansion will be the square terms of the type,

$$V = Ax_1^2 + By_1^2 + Cz_1^2 \qquad \ldots \quad (2)$$

where $C = -(A+B)$, since every term in the potential should satisfy Laplace's equation.

* The *initial* angle and the changes are measured in sexagesimal degrees

In general, the x, y, z axes of this rhombic part and those of the cubic part of the field will not coincide, though for our purposes, since the field is predominantly cubic, it would be convenient and sufficient to assume that the principal axes of the two coincide. If any lower type of symmetry is specifically required to explain experimental data we shall have to construct such a field by suitably orienting the two sets of axes.

There is also another factor which complicates the problem, namely, that the unit cell of the crystal will in general, contain more than one paramagnetic ion, and the crystalline field axes, associated with the different paramagnetic ions in the unit cell, will be oriented with respect to one another. These orientations cannot be always calculated since, detailed data regarding the dispositions of the atoms round the paramagnetic ions in the unit cell, are generally unavailable.

Now, the crystalline field axes associated with each paramagnetic ion will be uniquely determined by the dispositions of the negative charges in its neighbourhood and will remain unaffected if these dispositions are not disturbed. Actually, the paramagnetic ion and the neighbouring charged atoms form a closely bound group, due to the existence of strong binding forces between them, nearly as strong as in chemical bindings; as is evidenced by the large over-all separations, of the order of 20,000 cm.$^{-1}$ of the energy levels of the paramagnetic ions, produced by the electric fields due to those surroundings charged atoms. It is natural to think that such closely bound groups and, in consequence, the large electric fields round the paramagnetic ion might persist even in the state of solution and would thus offer a satisfactory explanation of the large deviations from the "free ion" behaviour observed in the aqueous solutions of many of the salts of the iron group,--deviations which are not only as large but of nearly the same magnitude as in the solid state.

The bindings between different such groups in the unit cell, however, may be relatively much weaker and there may, therefore, be appreciable changes in their relative positions with change of temperature. Even such changes should be very small as shown by the small thermal co-efficient of expansion of the crystals, of the order of 10^{-4} per degree, and in any case be in conformity with the symmetry requirements of the unit cell. The changes in the position of the atoms bound to the paramagnetic ion, due to changes of temperature, should be much smaller still.

Indeed, the magnetic observations themselves should offer a sensitive test of any such changes. Where the principal magnetic axes of the crystal are not determined uniquely by the symmetry of the crystal, as for example, the magnetic axes of a triclinic crystal, or the two axes in the (010) plane of a monoclinic crystal, any changes in the positions of these axes will give us a measure of the changes in the relative positions and orientations of the different paramagnetic groups in the unit cell. Experimentally it is found in the crystal of copper sulphate pentahydrate, which is triclinic and whose

unit cell contains two molecules of $CuSO_4$, $5H_2O$, there is hardly any change in the directions of the principal magnetic axes of the crystal in the temperature range studied. Again, in most of the monoclinic Tutton salts studied by us, containing two paramagnetic ions in the unit cell, there is very little change in the directions of the two principal magnetic axes χ_1 and χ_2 lying in the (010) plane, on passing from room temperature to about 80°K, as will be seen from the Tables I and II. Copper ammonium and copper potassium sulphates, nickel ammonium sulphate and cobalt ammonium fluberyllate are the few exceptions where an appreciable change in the directions of χ_1 and χ_2 occurs, mostly at temperatures above 150°K. For the first three crystals Bartlett (1932) also finds such changes of axes nearly of the same magnitude as ours, between +50°C and −50°C.

In those cases where the magnetic axes of the crystal do not change at all, as actually happens in most of the crystals, one can safely conclude that in the range of temperature noted the crystalline electric fields in the neighbourhood of the paramagnetic ions are practically unaffected by the changes in temperature. This is further corroborated by a detailed calculation of the crystal field constants which are found to remain practically independent of temperature in such cases as six co-ordinated nickel salts and four co-ordinated cobalt salts, where the conditions are particularly favourable for such a calculation.* Even when a considerable change in the magnetic axes of the crystals is observed, it may not indicate any change either in the magnitude or the asymmetry of the electric field associated with any particular paramagnetic ion. It may merely be due to the axes, associated with the different paramagnetic ions in the unit cell, changing their relative orientations, and this is presumably the reason for observed changes in the χ_1 and χ_2 axes of the few salts noted previously.

Detailed calculations of the crystalline field constants for nickel salts referred to above, further show that they not only are independent of the temperature, but also are of nearly the same magnitude in the different nickel salts, in which the immediate neighbours surrounding the nickel ion are the same; for example in all the Tutton salts of nickel or the highly hydrated sulphates and selenates of nickel, in which each Ni^{++} ion is surrounded by six water molecules occupying the corners of an octahedron with the Ni^{++} ion at the centre. From this point of view, it is not only the predominant cubic part of the field that will be determined by these immediate neighbours, but also the feeble rhombic part; the fields due to the distant atoms are regarded as negligible in comparison with even the feeble rhombic fields due to the immediate neighbours. We are aware that some of the earlier workers have attributed the large cubic part to the immediate neighbours and the feeble rhombic part to the influence of the distant atoms. But

* These will be published in later papers and may also be referred to in the memoir published by the author (1946).

there is already considerable evidence, especially, from the magnetic behaviour of these ions in aqueous solution, that the asymmetry of the electric field required to account for such behaviour is due to the immediate neighbours, and it may be presumed from the similarity of magnetic behaviour that this should be so in crystals also.

In any case, the assumption of the same crystalline fields in all the nickel salts, for example, or in all the cobalt salts, when the paramagnetic ions are surrounded by the same immediate neighbours, apart from its great plausibility considerably simplifies the discussions. It is, therefore, desirable to adopt this view unless we are forced by the experimental data to discard it. We may mention immediately that no experimental evidence available at present is inconsistent with this assumption.

It may be mentioned, finally, that there may also be another cause of this change in the orientation of the magnetic axes in addition to the changes caused by relative orientation of the different paramagnetic groups in the unit cell, as evidenced by the exceedingly high change in the value of "ψ" obtained in the crystal of ammonium chromium oxalate. It should be noted that this crystal as mentioned in the earlier papers has a very feeble paramagnetic anisotropy of only about $\frac{1}{4}\%$ and of the same order of magnitude as its diamagnetic anisotropy. In view of this not only the large change in ψ but also the small increase of anisotropy $\chi_1 - \chi_2$ as actually observed, are to be expected, since the large diamagnetic part of the anisotropy will be independent of temperature and the value of ψ will not be the same for the diamagnetic and the paramagnetic parts. From the nature of the variations at high temperatures it appears also that there is a critical point for these variations where they became maximum.

Further investigations at high temperatures are in progress at this laboratory to elucidate the nature of these changes in the magnetic axes of paramagnetic crystals.

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